(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 September 2002 (26.09.2002)

PCT

(10) International Publication Number
WO 02/075043 A1

BEST AVAILABLE COPY

(51) International Patent Classification[7]: D21C 1/02, 3/04

(21) International Application Number: PCT/US02/08339

(22) International Filing Date: 20 March 2002 (20.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/277,404 20 March 2001 (20.03.2001) US

(71) Applicant: **WISCONSIN ALUMNI RESEARCH FOUNDATION** [US/US]; 614 Walnut Street, P.O. Box 7365, Madison, WI 53707-7365 (US).

(72) Inventors: **AKHTAR, Masood**; 46 Waterford Circle, #101, Madison, WI 53719 (US). **SWANEY, Ross, E.**; 110 N. Spooner Street, Madison, WI 53705 (US). **HORN, Eric, G.**; 5802 Meadowood Drive, Madison, WI 53711 (US). **LENTZ, Michael, J.**; 308 S. Baldwin Street, Madison, WI 53703 (US). **SCOTT, Gary, M.**; 200 Scottholm Boulevard, Syracuse, NY 13224 (US). **BLACK, Cory, C.**; 2140 Cattail Run, #210, Gurnee, IL 60031 (US). **HOUTMAN, Carl, J.**; 226 Potter Street, Madison, WI 53705 (US). **KIRK, T., Kent**; 3245 Timber Lane, Verona, WI 53593 (US).

(74) Agent: **KETTNER, David, M.**; Quarles & Brady LLP, P.O. Box 2113, Madison, WI 53701-2113 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/075043 A1

(54) Title: METHOD FOR PRODUCING PULP

(57) Abstract: The present invention is a method for producing pulp from fibrous lignocellulose material using a treatment step which exposes the material to oxalic acid, or oxalic acid and sodium bisulfite, prior to pulping. The pulping of the resulting product requires less energy input and provides a pulp having enhanced physical properties as compared to untreated materials.

METHOD FOR PRODUCING PULP

CROSS-REFERENCE TO RELATED APPLICATIONS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

BACKGROUND OF THE INVENTION

[0001] In manufacturing paper from wood, the wood is first reduced to an intermediate stage in which the fibers in the wood are separated from their natural environment and transformed into a viscous liquid suspension called pulp. Of the various components of wood, the cellulose polymers are the most abundant and are the predominant molecules desired in the final pulp product. The second most abundant polymer, and least desirable pulp component, is lignin. Lignin is undesired because substantial amounts of lignin in pulp can deteriorate the smoothness of the final paper product and cause the paper to discolor when exposed to light. Lignin can also cause the pulp fibers to be rigid and weak.

[0002] Pulp may be produced from various types of woods using any one of several pulping techniques. The simplest of these techniques is the refiner mechanical pulping (RMP) method in which a mechanical milling operation grinds or abrades the wood in water until a desired state of freeness is achieved between its fibers. The RMP method is very efficient, typically converting approximately 95% of the dry weight of the wood into pulp. The RMP method, however, also leaves substantially all of the lignin in the pulp. As a result, RMP pulps generally provide low strength paper products having an opaque color. These paper products are generally used to manufacture newsprint or other low quality paper products.

[0003] Other pulping methodologies include thermo-mechanical pulping (TMP), chemical treatment with thermo-mechanical pulping (CTMP), chemi-mechanical pulping (CMP), and the chemical pulping, sulfate (kraft) or sulfite processes. In the chemical based methods, a chemical/water solution is generally used to dissolve the lignin and promote the separation of the

fibers. The absence of lignin, in turn, makes the final paper products stronger and less prone to discoloration. These products often include paper bags, shipping containers, printing and writing papers, and other products requiring strength.

[0004] In thermo-mechanical processes (e.g., TMP and CTMP), high temperatures are used to separate the fibers during refining. These processes generally require the refining to be carried out in one or more steps. The first step is usually a pressurized step with refining being performed at temperatures above 100°C and immediately below or at the softening temperature of lignin. During this step, the pulp is typically mechanically processed using the RMP method. In subsequent steps, the pressure and temperature is usually modulated to achieve the desired state of freeness between the fibers.

[0005] Relatively high total electric energy amounts or high quantities of input wood are required to produce pulps using the above mentioned pulping techniques. In particular, high energy inputs are generally required to obtain fiber separation in woods rich in lignin as such woods typically call for extended refining periods and high temperatures and/or pressures. Recent studies have also suggested that even thermal or chemical softening treatments of such woods does not guarantee a lower total energy consumption. This is because unprocessed fibers which are only mildly separated by the thermal or chemical treatments are difficult to fibrillate during the refining mechanical process.

[0006] Fibrillation is necessary to increase the flexibility of the fibers and bring about the fine material characteristics of quality processed pulp. In fact, it has been suggested that a decrease in the energy consumption from an established level in various TMP and CTMP processes has been associated with the deterioration of certain pulp properties, including a reduction in the long fiber content of the pulp, a lower tear strength and tensile strength, and a higher shives content. (See U.S. Patent No. 5,853,534, issued to Hoglund et al., Dec. 29, 1998). As a result, high energy consumption in TMP and CTMP processes has been generally necessary in today's pulping practices.

[0007] U.S. Patent No. 5,853,534 describes a method for producing pulp which attempts to overcome the above described energy consumption problem by performing mechanical or chemi-mechanical pulp in at least two steps. In the disclosed process, wood material is fed into a first refining step where it is mechanically processed at a temperature less than the softening temperature of lignin, and then fed into a second refining step where it is mechanically processed at a temperature exceeding the softening temperature of lignin. This process purports to guide fractures and fracture indications into the wood's fiber walls not rich in lignin during the first step to allow the fiber material to be separated with low energy inputs in areas rich in lignin during the second step. The process also purports to release fine material from areas between the initial fracture zone and the middle lamina of the fiber material rich in lignin during temperatures above the softening temperature of lignin, thus also lowering the total energy consumption in the process.

[0008] What is needed is an alternative method for producing pulp in an energy efficient manner which also improves paper strength properties while decreasing pollution.

BRIEF SUMMARY OF THE INVENTION

[0009] The present invention is a novel method for producing a pulp from a fibrous lignocellulose material using a pretreatment step which exposes the material to oxalic acid, or oxalic acid in combination with sodium bisulfite. Once treated, the material may be refined using any one of several pulping methods to produce a final pulp product.

[0010] In one embodiment, the method includes cooking the fibrous lignocellulose material at a temperature of between about 90°C and 140°C in a solution comprising oxalic acid prior to refining the material into a pulp. The dry weight amount of oxalic acid employed may be less than about 6%, or preferably less than about 5%, or more preferably between about .5% and 5%, or most preferably between about 1% and 3%, of the dry weight of the fibrous lignocellulose material. The treatment may be conducted at ambient pressures or higher, and for a period of time sufficient to allow the treated product to be later refined at reduced energy input

levels as compared to untreated materials, typically less than about 4 hours. Once treated, the treated material may then be refined to form a pulp used to produced a final paper product.

[0011] In a second embodiment, the method includes mixing the fibrous lignocellulose material with oxalic acid dihydrate crystals; pressurizing the mixture with steam of about 30 p.s.i.g. or less, or more preferably about 25 p.s.i.g.; defiberizing the material using a thermo-mechanical fiberizer; and refining the defiberized material to produce a pulp. The dry weight amount of oxalic acid employed may be less than about 6%, or preferably less than about 5%, or more preferably between about .5% and 5%, or most preferably between about 1% and 3%, of the dry weight of the fibrous lignocellulose material.

[0012] In yet another aspect of the invention, the method further comprises augmenting the oxalic acid solution, or oxalic acid dihydrate crystals, with sodium bisulfite to prevent the darkening of the material as it is processed. The dry weight amount of sodium bisulfite employed may be about 8% or less, or preferably between about 4% to 8%, more preferably between about 5% to 7%, and most preferably about 6% of the dry weight of the fibrous lignocellulose material.

[0013] One object of the present invention is to provide a method for producing pulp that is more energy efficient and less costly than standard pulping methods.

[0014] Another object of the present invention is to provide a method for producing pulp that has improved physical properties over pulps prepared using other conventional techniques.

[0015] It is one advantage of the present invention that paper produced from pulp manufactured in accordance with the disclosed method is stronger than other pulping methods, and results in a paper with a tear index of approximately 3.0 or more.

[0016] It is another advantage of the present invention that the combination of oxalic acid and sodium bisulfite provides a pulp with improved strength and minimal to no brightness penalty.

[0017] It is yet another advantage of the present inventions that the cooking liquor resulting from the present invention may be recycled and used in subsequent pretreatment processes.

[0018] Other features, advantages and objects will become apparent upon review of the specification, claims and drawing.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0019] None.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The present invention is a method for producing pulp from fibrous lignocellulose materials using a pretreatment step which exposes the material to oxalic acid, or oxalic acid and sodium bisulfite. In general, the pretreatment step includes heat treating the fibrous lignocellulose material (e.g., wood) in combination with oxalic acid, or oxalic acid and sodium bisulfite. Once treated, the material may be refined using any one of several pulping methods to produce a final pulp product.

[0021] The use of oxalic acid, or oxalic acid and sodium bisulfite, as described below, results in a pulp with improved physical properties which, in turn, provides enhanced physical properties in the final paper product. For example, the use of oxalic acid as a pretreatment to the pulp refining process results in a pulp that produces a paper product with improved strength properties. The use of oxalic acid and sodium bisulfite, on the other hand, results in a pulp that produces paper having improved strength with minimal to no brightness penalty.

[0022] The use of oxalic acid, or oxalic acid and sodium bisulfite, as described below, also provides an economic benefit to the pulping process. In particular, the use of either solution provides electrical energy savings when compared to conventional pulping processes. Their use may also result in material savings as the resulting pretreatment cooking liquors may be recovered and reused in subsequent applications. Although a detailed economic analysis has not

yet been performed, it is estimated that $7 million to $8 million dollars per year in energy costs and kraft pulp costs could be saved in a 200 ton per day operation operating 350 days per year.

[0023] Fibrous lignocellulose materials treated in accordance with the present invention are defined to generally include materials containing both cellulose polymers and lignin. These materials typically include matter capable of being processed into pulp for making paper products. Such materials may include, for example, hardwoods (i.e., broad-leafed species) and softwoods (i.e., conifers). More specifically, these materials may include the Southern Yellow Pines, Spruces, Western Hemlock, Aspens, and other smaller diameter trees. The material may also originate from either round wood (e.g., whole trees), residue (e.g., wood scraps left behind from forest and sawmill operations), or recovered paper. Recovered paper may include both pre-consumer recovered paper, such as trimmings and scraps from printing, carton manufacturing, or other converting processes which are reused to make pulp without reaching the final consumer, or post-consumer paper, such as corrugated boxes, newspapers, magazines, and office paper which has been recycled.

[0024] In general, prior to beginning the pretreatment process, the fibrous lignocellulose material is first reduced to a size appropriate for pulping, as is well known in the art. This will ensure that the material is sufficiently treated with the oxalic acid or with the oxalic acid and sodium bisulfite. In the preferred embodiment, the material to be treated is reduced to wood chips. It is anticipated, however, that the present method may also be effective with materials not reduced to wood chips, such as those materials derived from recovered paper or wood residues. It is also anticipated that the present method may also be effective in treating pulp.

[0025] In one embodiment, the fibrous lignocellulose material is heat treated in a solution having an amount of oxalic acid effective in improving the physical properties of the pulp and/or reducing energy input levels under the conditions described below. The amount of oxalic acid employed, as expressed in dry weight percentage, may be less than about 6%, or preferably less than about 5%, or more preferably between about .5% and 5%, or most preferably between about 1% and 3%, of the dry weight of the fibrous lignocellulose material.

[0026] Alternatively, the fibrous lignocellulose material may be mixed with oxalic acid dihydrate crystals, and subjected to thermo-mechanical processing. The amount of oxalic acid dihydrate crystals employed, as expressed in dry weight percentage, may be less than about 6%, or preferably less than about 5%, or more preferably between about .5% and 5%, or most preferably between about 1% and 3%, of the dry weight of the fibrous lignocellulose material.

[0027] The fibrous lignocellulose material may also be heat treated with oxalic acid, as described above, in combination with sodium bisulfite. The amount of sodium bisulfite employed, expressed in dry weight percentage, may be about 8% or less, or preferably between about 4% and 8%, or more preferably between about 5% and 7%, and most preferably about 6%, of the dry weight of the fibrous lignocellulose material.

[0028] The combined fibrous lignocellulose material and oxalic acid, or oxalic acid and sodium bisulfite, will generally be heat treated at ambient pressure or higher for a time sufficient to allow the treated product to be refined at reduced energy input levels, as compared to untreated materials, or refined to produce a pulp that provides a paper with improved strength, as compared to untreated materials. The temperature, time and pressure may vary from application to application as the machinery employed may differ in its functional characteristics, or because a skilled artisan may desire to obtain specific paper properties or processing parameters. A skilled artisan would be able to readily determine the optimal time, temperature and pressure for each particular application to arrive at the artisan's desired outcome.

[0029] The fibrous lignocellulose material and oxalic acid solution may, for example, be heat treated at a temperature of between about 90°C and 140°C, or preferably at a temperature of between about 90°C and 130°C, or most preferably at a temperature of between about 100°C or about 130°C. The cooking time may be between about 1 minute and about 4 hours, and more preferable between about 10 minutes and about 3 hours, but will depend primarily on the concentration of the oxalic acid in the solution, the temperature of the heat treatment and the pressure in the cooking chamber. The temperature range and the time period of the heat treatment may also vary depending upon the size of the fibrous lignocellulose material, the type

of fibrous lignocellulose material being treated, and the physical properties desired in the final pulp product.

[0030] The fibrous lignocellulose material and oxalic acid dihydrate crystals may, for example, be treated using a thermo-mechanical process. Under this method the material and oxalic acid dihydrate crystals would be subjected to a pressurized steam of about 30 p.s.i.g. or less, or more preferably about 25 p.s.i.g., while being sent through a thermo-mechanical refiner for fiberization.

[0031] After heat treating, the treated fibrous lignocellulose material is then washed and prepared for pulping. Many pulping methods are suitable for the present invention although mechanical pulping is preferred.

[0032] In its simplest form, a mechanical refining process is utilized. Dilution water is added to the treated material and the material is run through a mechanical refiner in a number of sequential passes. The number of passes of the treated material/pulp mixture will depend upon the freeness desired for the particular paper application to be made. Freeness is an arbitrary measure of water drainage. The treated material/pulp mixture is repeatedly fed through refiners until the desired level of freeness is achieved. Thus freeness may be periodically monitored to determine the progress of the pulps toward the freeness level which is desired for the paper. The pulp may also be dewatered as necessary between passes. Loblolly pine, treated using the procedures described above, requires between about 2 to 6 repeated passes to obtain a 100 ml CSF value in a single rotating 300 mm diameter disk atmospheric refiner.

[0033] The overall energy efficiency of the process can be compared with that of a standard process by pulping untreated material in the same apparatus while at the same time monitoring the energy consumption of the refining mill itself. As shown in the Examples below, the treated material requires significantly less energy input through the refiner to achieve the same level of freeness in the resulting pulps.

[0034] The pulps made through this procedure may then be made into paper using standard papermaking techniques. Standard techniques (as described by the Technical

Association of the Pulp and Paper Industry, TAPPI) known to work with refined pulps work equally well with pulps of the type created by the process described herein.

[0035] Paper made from the pulp prepared according to the present invention (treated pulp) can be compared in quality, strength and texture to that created using untreated material and standard pulping methods. Here, the treated pulp exhibits significantly increased strength property, thus indicating that the process of the present invention does not sacrifice the quality or strength of the paper in order to achieve the highly desirable energy savings. In fact, the present invention provides a unique combination of significant reduction in energy use with an increase in the strength properties of the resulting paper.

[0036] The details of the process of the present invention will become more apparent from the following Examples which describe the laboratory-scale utilization of the present process and the results achieved thereby. It is understood that the scale-up from a laboratory-scale to a plant-scale process of the pulping operation described below may involve some alteration of the parameters or details of the process steps described herein. It is to be understood that the Examples described below, while they demonstrate the efficacy and practicability of the process of the present invention, have not been optimized for a commercial scale.

[0037] Nevertheless, the experimental evidence presented makes it clear that the procedure is efficacious and efficient and enables the creation of commercial scale-procedures for implementing the general process described herein.

EXAMPLES

Example 1

[0038] Union Camp pine logs were obtained from Louisiana, chipped and then treated with a solution of oxalic acid in accordance with the present invention. Once treated, the chips were refined into a pulp, and the pulp used to prepare handsheets for testing.

Wood Preparation

[0039] Logs were debarked and chipped at U.S.D.A. Forest Products Laboratory (Madison, WI) to a nominal size of 6-14 mm. The chips were then placed in barrels and frozen to prevent the growth of contaminating microorganisms. The moisture content of the chips was measured to be approximately 48%.

Heat Treatment

[0040] Oxalic acid dihydrate from Sigma-Aldrich in a quantity of 69.04 grams per 1-kilogram was added with water to oven dried wood chips (5% oxalic acid to oven dried wood chips) at a liquor to wood ratio of about 4:1, respectively. A stationary digester was then used to cook several 1 kg samples of wood chips, oven dry basis, over varying temperatures and times, as is illustrated in Table 1. A Honeywell chart recorder was used to measure the cooking temperature. After cooking, the treated wood chips were washed thoroughly and frozen until refining.

Chip fiberization, pulp refining and handsheet production

[0041] The treated wood chips were refined to a pulp and then used to produce paper. Treated wood chips were first fiberized in a Sprout-Waldron Model D2202 single rotating 300 mm diameter disk atmospheric refiner. The feed rate through the refiner provided a power consumption level of between 10 kW and 15 kW. The refiner plate settings were 0.025 inch, 0.014 inch, 0.010 inch, and 0.008 inch.

[0042] Pulp was collected at each pass as hot water slurry. Between the passes the pulp slurry was dewatered to approximately 25% solids in a porous bag by vacuum. Dilution water at 85°C was then added each time as the pulp was fed into the refiner. Samples of the pulp were taken and tested for the Canadian Standard Freeness (CSF) and the process continued until the samples were refined to 100 CSF.

[0043] Energy consumption was measured using an Ohio Semitronic Model WH 30-11195 integrating Wattmeter attached to the power supply side of the 44.8 kW electric motor. The energy data from this experiment is listed in Table 1 and reported as percent energy savings. Hand sheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 1.

Table 1: Union Camp Pine Treatments

Sample Identification (°C / min / % oxalic acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.39	1.89	-----
90/30/5	0.40	1.94	2
90/60/5	0.33	2.56	4
90/90/5	0.40	2.46	9
90/120/5	0.45	2.43	6
90/150/5	0.48	2.33	9
90/180/5	0.60	2.20	19
95/90/5	0.60	2.52	23
95/180/5	0.76	3.42	19
100/30/5	0.40	1.90	5
100/90/5	0.72	2.95	16
100/180/5	0.84	3.83	23
105/60/5	NA	2.36	11
105/90/5	NA	2.91	25
105/120/5	NA	3.30	25
105/180/5	NA	3.38	25
110/30/5	0.56	1.94	4
110/90/5	NA	3.07	28
110/120/5	NA	3.16	26
120/30/5	0.64	2.32	12
130/10/5	0.59	2.19	9
130/20/5	0.72	2.63	15
130/30/5	0.74	2.66	15
140/30/5	0.77	2.17	10

N/A = Not available.

Example 2

[0044] Aspen wood chips were obtained from Stora Enso North America (Biron, Wisc.) (formerly, Consolidated Papers, Inc.) and treated with a solution of oxalic acid according to the

method described in Example 1. Varying times and temperatures were used as set forth in Table 2. Chips ranged from 6-10 mm. Moisture content was measured to be about 50%.

[0045] Once treated, the treated chips were refined to a pulp and then used to produce paper as described in Example 1. Energy consumption was measured as above and is reported in Table 2 as percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 2.

Table 2: Aspen Treatments

Sample Identification (°C / min / % oxalic acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.68	2.08	-----
90/60/5	0.67	2.13	11
90/90/5	0.67	2.08	17
95/60/5	0.65	2.07	19
100/60/5	0.66	2.22	39

Example 3

[0046] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0047] The chips were treated with a solution of oxalic acid as described in Example 1 which was augmented with either 75 grams of sodium bisulfite ("BIS") (approximately 6% BIS to oven dried wood chips), or 10 grams of BIS (approximately 1% BIS to oven dried wood chips). Varying times and temperatures were used as illustrated in Table 3. Once treated, the treated chips were refined to a pulp and then used to produce paper as described above. Energy consumption was measured and is reported in Table 3 as percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 3.

Table 3: Union Camp Pine Treatments with Sodium Bisulfite and Oxalic Acid

Sample Identification (°C / min / % oxalic acid + BIS)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)	ISO Brightness (%)
Control	0.47	2.05	-----	50.5
100/180/5	0.84	3.83	30	44.8
100/180/5 + 75g BIS[a]	0.78	3.98	26	49.7
100/180/5 + 75g BIS[b]	0.75	3.14	20	44.1
100/180/5 + 10g BIS[a]	0.72	3.03	11	45.7
100/180/75 g. BIS	0.71	2.18	11	51.0

[a]Oxalic acid and BIS mixed and cooked together

[b]BIS added after the cook

Example 4

[0048] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0049] The chips were then mixed with oxalic acid dihydrate crystals at a dry weight of either 5% or 1% of the chip's dry weight, and heat treated with steam pressurized to 25 p.s.i.g. for 1 minute and 15 seconds. During this time, the chips were sent through a thermo-mechanical refiner (Sprout-Bauer, model # 1210P, having a plate pattern D2B505, and 300-mm diameter) for fiberization.

[0050] The subsequent fiber stock was further developed using the atmospheric refiner mechanical pulping process as described in Example 1. Once refined, the prepared pulp was used to produce paper as previously described. Energy consumption was measured as above and reported in Table 4 as percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 4.

Table 4: Use of Oxalic Acid for Thermo-mechanical Pulping

Sample Identification (% oxalic acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.55	2.55	------
5% Oxalic Acid	0.60	2.55	33
1% Oxalic Acid	0.58	2.53	20

Example 5

[0051] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0052] The chips were then treated with supplementary cooking acids, hydrochloric acid and sulfuric acid, to determine whether the cooking acids effectively promote electrical energy savings or improvements in paper strength when used under the treatment protocols of the present invention. Solutions of sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), having concentrations equivalent to the pH of a standard solution of oxalic acid, were added to oven dried wood chips at a liquor to wood ratio of about 4:1, respectively. A stationary digester was used to cook several 1 kg samples of wood chips, oven dry basis, over varying temperatures and times.

[0053] After cooking, the treated chips were refined to a pulp and used to produce paper as described in Example 1. Energy consumption was measured as above and reported in Table 5 as percent energy savings. Hand sheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 5.

Table 5: Treatment with sulfuric or hydrochloric acid

Sample Identification (acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.68	2.08	-----
HC1	0.54	2.61	12
H_2SO_4	0.50	2.29	16

Example 6

[0054] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0055] The chips were treated with oxalic acid of varying amounts (3%, 2%, 1%, and 0.5% per 1-kilogram of oven dried wood chips) according to the method described in Example 1. Varying times and temperatures were used as illustrated in Table 6. Once treated, the chips were refined to a pulp and used to produce paper as above. Energy consumption was measured as above and reported in Table 6 as percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 6.

Table 6: Union Camp Pine Treatments

Sample Identification (°C / min / % oxalic	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.47	2.05	-----
130/10/1	0.70	2.94	22
130/10/2	0.74	3.19	30
130/10/3	0.81	3.61	32
130/20/1	0.69	3.07	26
130/30/1	0.71	3.16	27
130/30/0.5	0.63	2.34	18
130/60/0.5	0.63	2.33	16
130/90/0.5	0.61	2.40	15
140/10/1	0.83	3.44	32
140/10/2	0.89	3.91	24
140/10/3	0.93	4.12	30

Example 7

[0056] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0057] The chips were then treated with oxalic acid of varying amounts (3%, 2%, and 1% per 1-kilogram of oven dried wood chips) according to the method described in Example 1. Varying times and temperatures were used as illustrated in Table 7. After cooking, the treated chips were washed thoroughly and frozen until refined in a thermo-mechanical pulping (TMP) process.

[0058] As part of the TMP process, the treated wood chips were pressurized with steam to 25 p.s.i.g. for 1 minute and 15 seconds. During this time the chips were sent through a

thermo-mechanical refiner (Sprout-Bauer, model # 1210P, plate pattern D2B505, 300 mm diameter) for fiberization at a plate gap setting of 0.029 inch.

[0059] The subsequent fiber stock was further developed through an atmospheric refiner mechanical pulping (RMP) process and then used to produce paper. The RMP process was performed using a Sprout-Waldron Model D2202 single rotating 300 mm diameter disk atmospheric refiner. The fiber stock was fed through the refiner at a rate such that a power consumption level of between 10 kW and 15 kW was produced. The refiner plate settings were 0.025 inch, 0.014 inch, 0.010 inch, and 0.008 inch.

[0060] Pulp was collected at each pass as hot water slurry. Between passes the pulp slurry was dewatered to approximately 25% solids in a porous bag by vacuum. Dilution water at 85°C was added each time as the pulp was fed into the refiner. Samples of the pulp were then taken and tested for their CSF value and the process continued until the samples were refined to 100 CSF.

[0061] Energy consumption was measured using an Ohio Semitronic Model WH 30-11195 integrating Wattmeter attached to the power supply side of the 44.8 kW electric motor. The energy data from this experiment is listed in Table 7 and reported in percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The handsheets were also analyzed for their brightness as compared to handsheets prepared using pulp produced through a conventional RMP process and a conventional TMP process. The results from this testing are also reported in Table 7.

Table 7: Union Camp Pine Treatments

Sample Identification (°C / min / % oxalic acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)	ISO Brightness (%)
Control	0.62	2.42	-----	51.1
130/10/1	0.74	3.15	26	47.5
130/10/2	0.78	3.24	32	46.2
130/10/3	0.88	3.97	36	45.3

[0062] These results were further compared to the loss in brightness experienced by paper produced using pulp that was subject to a fungal pretreatment process. Normally, fungal pretreatment and/or chemical modification processes result in the darkening of the pulp and a reduced brightness in the final paper product. Here, oxalic acid treated chips fiberized by TMP darkened less than the same wood chips fiberized by RMP (Table 8), and significantly less than chips subjected a fungal pretreatment and fiberized by TMP or RMP. (Table 9).

Table 8: Oxalic Acid Treated Union Camp Pine Paper Brightness

Refining Type	Control (%)	Treatment (%)	Difference (%)
RMP (Refiner Mechanical Pulping)	50.5	46.7	4.4
TMP (Thermomechanical Pulping)	51.1	47.5	3.6

Table 9: Fungal Pretreated Union Camp Pine Paper Brightness

Refining Type	Control (%)	Treatment (%)	Difference (%)
RMP (Refiner Mechanical Pulping)	50.5	40.0	10.5
TMP (Thermomechanical Pulping)	51.1	35.8	15.3

Example 8

[0063] Wood chips were treated in accordance to the method of the present invention and the cooking liquor recycled to determine whether or not it could be recovered and reused.

[0064] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0065] The chips were cooked at 130°C for 10 minutes in 41.42 grams of oxalic acid per 1-kilogram oven dried wood chips (approximately 3% oxalic acid to oven dried wood chips) according to the method described in Example 1. After cooking, wood chips were washed thoroughly and frozen until refining. The cooking liquor was collected after each cook and reused following an augmentation with approximately 20.71 grams (50%) of the initial oxalic acid.

[0066] Once treated, the chips were refined to a pulp and used to produce paper as described in Example 1. Energy consumption was measured as described and is reported in Table 10 as percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 10, wherein Recycle 4 and Recycle 5 indicate recycled cooking liquor augmented and used for the fourth and fifth time, respectively.

Table 10: Union Camp Pine Treatments

Sample Identification (°C / min / % oxalic acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.62	2.42	-----
130/10/3	0.79	3.57	27
130/10/3 Recycle 4	0.79	3.52	25
130/10/3 Recycle 5	0.81	3.42	24

Example 9

[0067] Wood chips were heat treated at 130°C for 10 minutes in an amount of oxalic acid approximate to 1.5% oxalic acid (dry weight) to oven dried wood chips, in order to determine if the treatment provided equivalent electrical energy savings and improved paper strength as compared to wood chips treated using recycled cooking liquor, as described in Example 8, and to determine the optimal amount of oxalic acid needed to maintain electrical energy savings and improved paper strength using recycled cooking liquor.

[0068] Union Camp pine logs were obtained from Louisiana, chipped and stored according to the method described in Example 1. The moisture content of the chips was measured to be approximately 48%.

[0069] The chips were cooked at 130°C for 10 minutes in 20.71 grams of oxalic acid per 1-kilogram oven dried wood chips (approximately 1.5% oxalic acid to oven dried wood chips) according to the method described in Example 1. Once treated, the chips were refined to a pulp and used to produce paper as described in Example 1. Energy consumption was measured as described and is reported in Table 11 as percent energy savings. Handsheets were also prepared and tested using TAPPI standard testing methods. The results from this testing are also reported in Table 11.

Table 11: Union Camp Pine Treatments

Sample Identification (°C / min / % oxalic acid)	Burst (kN/g)	Tear (mN-m^2/g)	Energy Savings (%)
Control	0.62	2.42	-----
130/10/1.5	0.72	3.11	26

[0070] Comparing these results with the data illustrated in Table 10 above indicates that improvements in paper strength are obtained using a recycled cooking liquor which has been augmented to percent ratio of 3% oxalic acid to oven dried wood chips, as compared to wood chips heat treated in fresh oxalic acid at about 1.5%.

CLAIM OR CLAIMS

WE CLAIM:

1. A method for pulping a fibrous lignocellulose material, the method comprising the steps of:

(a) reducing the material to a size appropriate for pulping;

(b) treating the reduced material in combination with oxalic acid; and

(c) mechanically refining the treated material into a pulp.

2. The method of Claim 1 wherein the oxalic acid is at an amount less than about 6 % of the dry weight of the reduced material.

3. The method of Claim 1 wherein the oxalic acid is at an amount less than about 5 % of the dry weight of the reduced material.

4. The method of Claim 1 wherein the oxalic acid is at an amount between about 0.5 % and about 5 % of the dry weight of the reduced material.

5. The method of Claim 1 wherein the oxalic acid is at an amount between about 1 % and about 3 % of the dry weight of the reduced material.

6. The method of Claim 1 wherein the reduced material is further treated with sodium bisulfite.

7. The method of Claim 6 wherein the sodium bisulfite is at an amount of about 8% or less of the dry weight of the reduced material.

8. The method of Claim 6 wherein the sodium bisulfite is at an amount between about 4% and about 8% of the dry weight of the reduced material.

9. The method of claim 6 wherein the sodium bisulfite is at an amount between about 5% and about 7% of the dry weight of the reduced material.

10. The method of claim 6 wherein the sodium bisulfite is at an amount of about 6% of the dry weight of the reduced material.

11. The method of Claim 1 wherein the treated material is refined using either a mechanical pulping method or a thermo-mechanical pulping method.

12. The method of Claim 1 wherein the material is treated at a temperature of between about 90°C and about 140°C.

13. The method of Claim 1 wherein the material is treated at a temperature of between about 90°C and about 130°C.

14. The method of Claim 1 wherein the material is treated at a temperature of between about 100°C and about 130°C.

15. The method of Claim 1 wherein the fibrous lignocellulose material is a either a wood or a recovered paper.

16. A method for producing pulp from a fibrous lignocellulose material, the method comprising the steps of:

(a) reducing the material to a size appropriate for pulping;

(b) mixing the reduced material with oxalic acid dihydrate;

(c) treating the mixture with steam;

(d) defiberizing the treated material using a thermo-mechanical fiberizer; and

(e) mechanically refining the defiberized material to produce a pulp.

17. The method of Claim 16 wherein the oxalic acid dihydrate is at an amount less than about 6 % of the dry weight of the reduced material.

18. The method of Claim 16 wherein the oxalic acid dihydrate is at an amount less than about 5 % of the dry weight of the reduced material.

19. The method of Claim 16 wherein the oxalic acid dihydrate is at an amount between about 0.5 % and about 5 % of the dry weight of the reduced material.

20. The method of Claim 16 wherein the oxalic acid dihydrate is at an amount between about 1 % and about 3 % of the dry weight of the reduced material.

21. The method of Claim 16 wherein the reduced material is further mixed with sodium bisulfite.

22. The method of Claim 21wherein the sodium bisulfite is at an amount of about 8% or less of the dry weight of the reduced material.

23. The method of Claim 21 wherein the sodium bisulfite is at an amount between about 4% and about 8% of the dry weight of the reduced material.

24. The method of claim 21 wherein the sodium bisulfite is at an amount between about 5% and about 7% of the dry weight of the reduced material.

25. The method of claim 21 wherein the sodium bisulfite is at an amount of about 6% of the dry weight of the reduced material.

26. The method of claim 16 wherein the mixture is steam heated at a pressure of less than about 30 p.s.i.g.

27. The method of claim 16 wherein the mixture is steam heated at a pressure of about 25 p.s.i.g.

28. The method of Claim 16 wherein the defiberized material is refined using either a mechanical pulping method or a thermo-mechanical pulping method.

29. The method of Claim 16 wherein the fibrous lignocellulose material is a either a wood or a recovered paper.

SEQUENCE LISTING

Not applicable.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/08339

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :D21C 1/02, 3/04
US CL :162/20, 25, 76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/20, 25, 76

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

West

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,599,138 A (LINDAHL) 08 July 1986, see 5, lines 38-64.	1-29
Y	US 5,306,392 A (MITA) 26 April 1994, see column 8, lines 4-17.	2-5, 17-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search 07 MAY 2002	Date of mailing of the international search report 17 JUN 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer STEVE ALVO Telephone No. (703) 308-0651

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